

UDC 553.612:66.081.3:665.3

## EXTRUSION MOLDING OF KAOLIN SORBENTS

V. Yu. Prokof'ev,<sup>1</sup> P. B. Razgovorov,<sup>1</sup> K. V. Smirnov,<sup>1</sup> E. A. Shushkina,<sup>1</sup> and A. P. Il'in<sup>1</sup>Translated from *Steklo i Keramika*, No. 8, pp. 29–32, August, 2007.

The properties of kaolin molding pastes containing modifying additives with different acid-basic properties were investigated. Addition of liquid glass significantly improves the structural-mechanical properties of the systems and increases the mechanical strength of the finished granulated sorbent. Preliminary modification of liquid glass with carbamides negatively affects the moldability of the kaolin pastes. Treatment of kaolin with acetic acid followed by dissolution of the paste with liquid glass decreases the extrudability; on the other hand, the volume of the open pores in the absorbent increases from 0.15–0.22 to 0.27–0.40 cm<sup>3</sup>/g.

In the 1980s, a trend toward recycling of natural sorbents was observed in the cycle for purifying food and mineral oils [1]. In particular, aluminosilicate materials, especially kaolins, should be distinguished as some of the most accessible sorbents. The purification process is conducted due to hydrogen bonds [2], whose formation is determined by the presence of protons from the rock-forming minerals in the sorbent material.

However, it is well known that kaolins have a low specific surface area which increases insignificantly even during intensive grinding. To increase the absorptivity of these sorbents, it is frequently necessary to modify the surface with mineral or organic acids, which increases its affinity for the component extracted. In addition, natural aluminosilicates are usually added to the system in the form of insoluble powders and filtration is then required. The use of granulated sorbents is promising, since this makes it possible to simplify the existing purification technology. However, we must not forget that incorporation of an acid agent in the aluminosilicate molding paste will negatively affect the extrudability of the system [3]. Mechanical strength is also an important parameter of sorbent granules. Traditional high-temperature calcination is undesirable in this case, since it can significantly decrease the already insignificant specific surface area and porosity of the investigated material.

Preliminary experiments showed that in oil medium, in contrast to water, even uncalcined kaolin granules are sufficiently resistant to destruction. Liquid glass (LG) can additionally be used to increase their strength. This additive is selected because it improves the moldability of the system and by producing a pronounced alkaline reaction, it is traditionally used to reduce the acid number of oil-containing media.

We investigated the stage of extrusion molding of kaolin pastes containing readily available modifiers with different acid-basic properties in production of sorbents for food and mineral oils.

Kaolin (Samara Oblast, TU 5729-016-48174985–2003) was used as the initial feedstock; according to the findings of x-ray phase analysis, it contains kaolinite with  $\beta$ -quartz impurity (Fig. 1) and Fe<sub>2</sub>O<sub>3</sub> (0.02%).<sup>2</sup> The granulometric composition of the kaolin is as follows (%): 0–0.5  $\mu$ m, 0.28; 0.5–1.2  $\mu$ m, 3.21; 1.2–2.5  $\mu$ m, 8.84; 2.5–5.0  $\mu$ m, 15.16; 5.0–10.0  $\mu$ m, 23.28; 10.0–20.0  $\mu$ m, 34.77; 20.0–30.0  $\mu$ m, 10.76; 30.0–40.0  $\mu$ m, 3.73. Sodium LG (29.0% SiO<sub>2</sub>, 8.9% Na<sub>2</sub>O, remainder H<sub>2</sub>O) had a density of 1.42 g/cm<sup>3</sup> and silicate ratio of 3.3.

<sup>2</sup> Hear and below — the weight content.

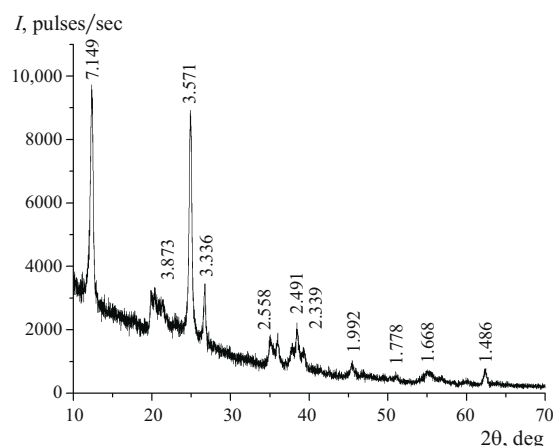
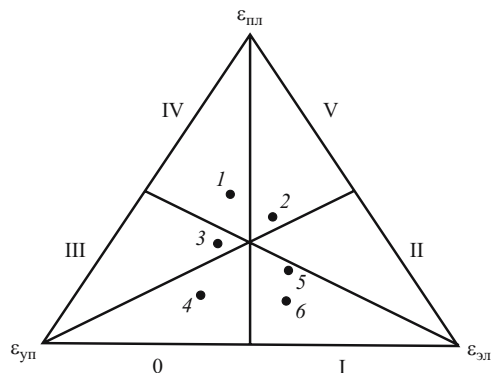


Fig. 1. X-ray diffraction pattern of kaolin from Samara deposits (CuK $\alpha$  radiation, the interplanar distances are indicated in Å).

<sup>1</sup> Ivanovo State Chemical Engineering University, Ivanovo, Russia.



**Fig. 2.** Diagram of evolution of strains in kaolin molding pastes. Disperse medium: 1 – 3) kaolin; 4 – 6) kaolin treated with AA. Dispersion medium: 1, 4) water; 2, 5) LG; 3, 6) LGC.

The molding pastes were prepared as follows. Kaolin was mixed with water (Sample 1), LG (Sample 2), or LG modified with carbamide at 70°C (LGC, Sample 3) until a homogeneous plastic paste formed. The dispersion medium in these samples was respectively 28.5, 31.5, and 33.0%. The kaolin was also first treated with 70% acetic acid (AA) with a S : L ratio of 5 : 1 and after drying, treatment with these reagents was repeated (samples 4 – 6). Inclusion of the liquid phase was at 15.5% (kaolin – AA – water, Sample 4), 28.5% (kaolin – AA – LGC, Sample 6), with Sample 5 (kaolin – AA – LG) in the middle at 18.0%. The samples had the optimum molding moisture content, monitored according to the recommendations in [3, 4]. The granules were dried at 110 – 115°C for 4 h.

The structural-mechanical properties were measured on an instrument designed by D. M. Tolstoi. The results were processed with the method in [3, 4]. The molding pastes were tested on a Rheotest-2 rotary viscometer. The flow curves were obtained in the shear rate range of 2 – 4800 sec<sup>-1</sup> and used to determine the rheological characteristics [3 – 5]. The IR spectra were made on an Avatar

360 FT – IR ESP in the 4000 – 500 cm<sup>-1</sup> wavenumber region. The absorption spectra were interpreted with the data in [6].

As the experimental data show (see Table 1 and Fig. 2), the molding paste prepared from kaolin mixed with water (Sample 1) belongs to structural-mechanical type IV with predominant development of plastic strains. The high plasticity value and brief relaxation period of the system should be noted. In addition, the paste has a strong coagulation structure and is characterized by a comparatively low flow index, which allows fabricating articles of almost any geometric shape by extrusion [3, 5]. However, the granules obtained have low mechanical strength (approximately 0.5 MPa). Replacement of the aqueous dispersion medium by LG (Sample 2) turned the system into structural-mechanical type V, where slow elasticity predominates over fast elasticity. This is also indicated by the decrease in the plasticity of the system with a simultaneous increase in its elasticity and relaxation period. It is necessary to note that the strength of the coagulation structure increases by more than two times while the flow index decreases to 0.3. On the whole, the observed changes in the properties of the paste favorably affect the extrudability of articles of complex shape [3, 5]. The mechanical strength of the granules increases sharply, attaining 8 – 9 MPa.

The use of LGC (Sample 3) for making the molding paste yields a system of structural-mechanical type I with predominance of fast elastic strains. In addition, an important decrease in the strength of the coagulation structure is observed, and the flow index decreases to 0.2. Although this tendency is unfavorable, the absolute values of the structural-mechanical and rheological properties of such a molding paste are almost optimum [3]; the mechanical strength of the granules is 1.5 – 2.0 MPa.

Mixing kaolin previously modified with AA with water (Sample 4) sharply decreases the plastic parameters of the molding paste in comparison to the untreated feedstock

**TABLE 1**

Sample	Dispersion medium	Structural-mechanical characteristics			Rheological characteristics			
		plasticity, 10 <sup>-6</sup> sec <sup>-1</sup>	elasticity	relaxation period, sec	total power for flow, MW/m <sup>3</sup>	power for destruc- tion of coagulation structure, MW/m <sup>3</sup>	consistency constant, Pa · sec	flow index
Disperse medium — kaolin								
1	Water	3.7	0.5	500	38.9	12.1	214.2	0.4
2	Liquid glass	2.8	0.6	550	56.5	28.4	994.7	0.3
3	Liquid glass modified with carbamide	2.5	0.4	600	25.9	7.4	980.7	0.2
Disperse medium — kaolin treated with acetic acid								
4	Water	0.4	0.6	2100	41.6	15.3	252.3	0.4
5	Liquid glass	2.1	0.7	650	50.0	22.3	970.7	0.2
6	Liquid glass modified with carbamide	1.9	0.7	750	17.2	5.6	667.2	0.2

(Sample 1), so that the system belongs to structural-mechanical type zero with pronounced predominance of fast elastic strains. An important increase in the relaxation period is also characteristic of it. However, the high strength of the coagulation structure should be considered a positive point. This molding paste is thus only suitable for extrusion of granules of simple geometric shape [3], and their mechanical strength is only 0.5 MPa. In LG medium (Sample 5) and LGC medium (Sample 6), the molding properties of the pastes improve significantly. These pastes belong to structural-mechanical type I, have relatively high plasticity and a brief relaxation period, and retain high strength of the coagulation structure and a low flow index, which is favorably reflected in their extrusion properties [3]. However, the mechanical strength of the granules remains low (approximately 1 MPa).

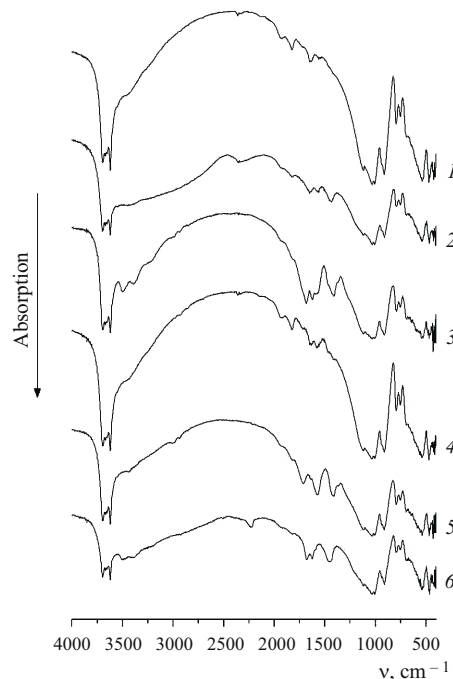
Modification of kaolin with AA thus negatively affects the extrusion properties of the molding pastes and the mechanical strength of the granules. On the contrary, use of LG has a positive effect with respect to both the moldability and the mechanical strength of the finished product.

The causes of such rheological behavior of the systems can be found with the data from IR spectroscopy of the samples (Fig. 3).

Intrasurface hydroxyl groups at the apices of the kaolinite octahedrons are characterized by individual structural properties that distinguish them from neighboring OH groups. This complicates the spectrum of kaolinite in the region of OH stretching vibrations, in particular, splitting of the band in the region of  $3710 - 3620 \text{ cm}^{-1}$ , and the low-frequency maximum at  $3620 \text{ cm}^{-1}$  should be assigned to vibrations of internal hydroxyl groups [7].

The band at  $538 \text{ cm}^{-1}$  probably corresponds to mixed deformation vibrations of Si-O and Al-O(H), while the presence of a low-intensity band at  $1634 \text{ cm}^{-1}$  indicates possible condensation of the surface and internal hydroxyl groups in kaolinite, which results in formation of the polymer-hydrate form of water [8]. When LG is incorporated in the kaolin-water system, the maximum of this band is shifted to the short-wave region,  $1652 \text{ cm}^{-1}$  (Sample 2), which indicates the presence of  $\text{H}_3\text{O}^+$  ions in it. In this case, breaking of the O-H bond in the structural hydroxyl groups in the octahedral network of the kaolinite layer and the appearance of hydroxonium ions in the product of the reaction with LG. The absorption intensity increases (by 1.7 times) and the structure of the OH groups of the initial kaolin material is destroyed. Proton recombination on bonds and the subsequent structural changes should cause formation of amorphous silicon and aluminum oxides, which probably also directly affects the sorption properties of the reaction product obtained. The absorption also decreases in the  $540 - 538 \text{ cm}^{-1}$  region (by 1.8 times), corresponding to mixed Si-O and Al-O(H) deformation vibrations.

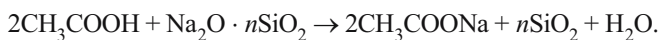
The slight shift of the absorption bands at  $1118 \text{ cm}^{-1}$  (asymmetric Si-O stretching vibrations),  $1031 \text{ cm}^{-1}$  (Al-OH, octahedral layers of  $\text{Al}^{3+}$  with  $\text{O}^{2-}$  and  $\text{OH}^-$ ) to the long-wave region ( $1120$  and  $1033 \text{ cm}^{-1}$ , respectively) char-



**Fig. 3.** IR spectra of kaolin molding pastes: Disperse medium: 1 – 3) kaolin; 4 – 6) kaolin treated with AA. Dispersion medium: 1, 4) water; 2, 5) LG; 3, 6) LGC.

acteristic of Sample 5 could be due to its partial dealumination. The intensity of these absorption bands in comparison to the absorption bands of Sample 1 decreases very insignificantly. The degree of crystallinity of kaolin probably remains almost unchanged as a result of its activation by acetic acid.

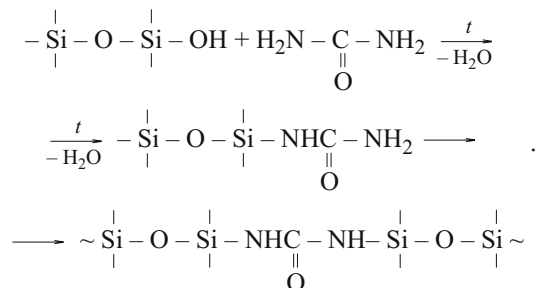
The presence of a peak at  $1575 \text{ cm}^{-1}$  acts as a marker of  $\text{COO}^-$  carboxylate ions in the kaolin-AA-water system (Sample 4), and the number of these anions is much lower (approximately 77% lower) than in the system of acid-activated kaolin subsequently mixed with LG (peak at  $1573 \text{ cm}^{-1}$ ). This is probably due to the fact that acetic acid can form acetate salts with sodium silicate (LG) and simultaneously form silica gel according to the reaction:



An excess of concentrated AA in the kaolin-AA-LG system (Sample 5) also causes dimerization of the carboxyl group (characteristic peak at  $1714 \text{ cm}^{-1}$ ).

The analysis of the IR spectrum of Sample 6 (kaolin-AA-LGC) indicates the absence of carboxylate anions in the system. Actually, in the case of formation of a  $-\text{COO}-$  group, the characteristic frequency of carbonyl absorption ( $1683 \text{ cm}^{-1}$ ) would disappear due to resonance between the two  $-\text{CO}-$  bonds, and symmetric and asymmetric vibrations would appear at the same wavenumbers ( $1537$  and  $1411 \text{ cm}^{-1}$ ) as in Sample 5. On the contrary, the shift of the frequency of C-N stretching vibrations of the carbamide

molecules ( $1480 - 14350 \text{ cm}^{-1}$ ) to the  $1408 \text{ cm}^{-1}$  region and the appearance of the characteristic absorption band of a bound NH group ( $3388 \text{ cm}^{-1}$ ) suggest that carbamide exists in the system in the form of a binder with LG obtained with a polycondensation reaction [9]:



This is also indirectly confirmed by broadening of the fragment in the  $1408 \text{ cm}^{-1}$  region, which can be interpreted by the imposition of the vibrations of C — N and the out-of-plane vibrations of the NH bond. The characteristic peak contained in the  $1600 - 1570 \text{ cm}^{-1}$  frequency range also indicates formation of carbamide salt [6].

The main difference between the IR spectrum of the kaolin — AA — GLC system and the spectrum obtained without AA activation consists of the presence of a peak at  $2230 \text{ cm}^{-1}$  and the low-intensity band at  $2508 \text{ cm}^{-1}$ . This could be due to the fact that carbamide already bound with LG according got the reported scheme blocks formation of its sodium salt with acetic acid. This is particularly indicated by the absence of a band at  $1573 \text{ cm}^{-1}$  (COO anion)) characteristic of Sample 3. The absorption bands in the  $2508$  and  $2230 \text{ cm}^{-1}$  region are most probably “aluminum” bands [6], which probably indicates that the free part of the carbamide can exhibit both alkaline and acid properties and react with the acid surface of kaolin by participating in the protonation process.

Based on the IR spectroscopic data, the important improvement in the properties of molding pastes made of kaolin using LG can be attributed to destruction of the OH groups in kaolinite and formation of hydroxonium ions on the surface of particles of the solid phase. Preliminary modification of LG with carbamide at high temperatures probably causes polycondensation [9], which also alters the structural-mechanical and rheological characteristics of the mix-

tures with kaolin. In turn, the sharp change in the properties of the kaolin pastes treated with AA is most probably due to formation of acetates and silica gel, which determines a different character of the coagulation reaction of the particles.

However, when AA is added to the kaolin mixture and subsequently mixed with liquid glass, the volume of open pores increases from  $0.15 - 0.22$  and  $0.27 - 0.40 \text{ cm}^3/\text{g}$ , which increases the sorption capacity of the sorbent. The peroxide number of the oil-containing system decreases by  $10 - 40\%$  and the content of metal (copper and iron) cations in the oil decreases by  $2 - 5$  times after contact with the finished granulated sorbent.

Incorporation of liquid glass to kaolin molding pastes thus significantly improves their structural-mechanical and rheological properties. The mechanical strength of the granules increases by more than one order of magnitude.

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